Quantum critical end point of the Kondo volume collapse

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The Kondo volume collapse describes valence transitions in f-electron metals, and is characterized by a line of first order transitions in the pressure-temperature phase plane terminated at critical end points. We analyze the quantum critical end point, when the lower end point is tuned to $T = 0$, and determine the specific heat, thermal expansion, and compressibility. We find that the inclusion of quantum critical fluctuations leads to a novel bifurcation of the first order phase line. Finally, we show that critical strain fluctuations can cause both, superconductivity and non-Fermi liquid behavior near the critical point.

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Quantum criticality in heavy fermion materials is predominantly discussed in the context of magnetic phase transitions[1]. In contrast, instabilities in the charge sector, which are well known to occur in Ce and Yb based intermetallics, are usually first order transitions. In the case of strong first order transitions, like the Kondo volume collapse (KVC) transition between α and γ Ce [2] or the related behavior in $YbInCu_4$ [3], critical fluctuations are irrelevant. However, theories [4, 5] and experiments [6] for the KVC yield a line of first order phase transitions in the pressure-temperature phase plane that is terminated at critical points on the high and (sometimes) on the low temperature end. The location of this lower end point is tunable. For example, a suppression of the volume collapse transition was achieved by alloying Ce with Th [6] or by applying an external magnetic field to $Ce_{0.8}La_{0.1}Th_{0.1}$ [7]. In the case where the lower end point is tuned to $T = 0$, a quantum critical end point emerges.

In this paper we investigate the behavior in the vicinity of the quantum critical end point of the Kondo volume collapse. As shown in Fig. 1, we demonstrate that the $p{-}T$ phase transition line is qualitatively changed by critical fluctuations. In addition, we determine the pressure and temperature dependence of the heat capacity, the compressibility, and the thermal expansion, and discuss the possibility of superconductivity and non-Fermi liquid behavior caused by these critical fluctuations. Ce and Yb based intermetallic alloys with a moderate high temperature bulk modulus are good candidates to identify such a quantum critical point of the Kondo volume collapse, where the critical fluctuations are in a universality class similar to that of a metamagnetic end point[8]. Being in the charge sector, KVC fluctuations may serve as a mechanism for s-wave superconductivity [9, 10]. Strong retardation effects of the critical pairing interaction are important and enhance the superconducting transition temperature as compared to a BCS calculation. Our predictions for the temperature dependence of the compressibility and the thermal expansion are unique for the quantum critical end point of the Kondo volume collapse. Identifying such a behavior in a superconducting material strongly suggests that the pairing is due to critical strain fluctuations. Finally, recent advances in the theory of quantum phase transitions in metallic systems[11] demonstrate that previous results obtained for magnetic critical points are unstable against non-analytic corrections to the collective mode dynamics. Quantum criticality in the charge sector, as discussed in our paper, is therefore one of the very few cases where robust predictions for non-Fermi liquid behavior can be made.

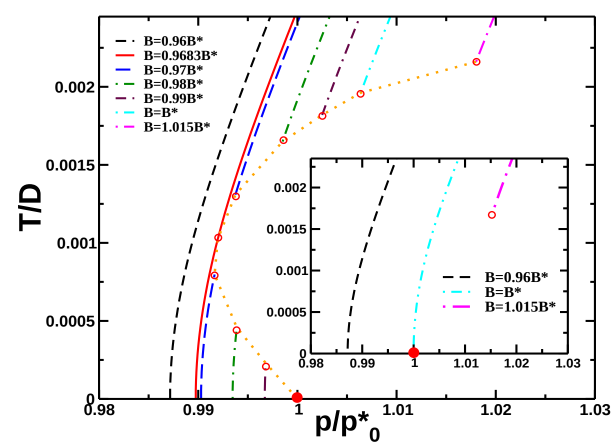

FIG. 1: Pressure-temperature phase diagram for the KVC model for different values of the bare bulk modulus B from the slave boson theory (see text). The main figure includes critical fluctuations, the inset is the mean field result. Lines represent first order transitions from a low T_K phase, to the left of the line, to a high T_K phase, to the right of the line (this is for Ce alloys, the reverse would be true for Yb ones). The solid circles and dot indicate critical end points for $T > 0$ and $T = 0$, respectively. The inclusion of fluctuations causes the first order line to "bifurcate" for $B < B^*$. The lower line then terminates at a quantum critical end point for $B = B^*$.

A candidate for this behavior is $CeCu_2Si_{2-x}Ge_x$ under

pressure [12]. A volume discontinuity at $p \simeq 15$GPa was observed in $CeCu_2Ge_2$ [13]. Evidence for a valence instability in $CeCu_2Si_2$ at pressure $p \simeq 25$kbar was already given in Ref. 14. The increase of the residual resistivity and the drop of the T^2 coefficient of the low temperature resistivity with pressure in $CeCu_2Si_2$ and $CeCu_2Ge_2$ have been interpreted in terms of critical valence fluctuations [10, 15]. Also, the ability to separate two superconducting regimes by varying pressure in $CeCu_2Si_{1.2}Ge_{0.8}$ [12] supports the point of view that two different mechanisms are at work, one related to the magnetic critical point and the other to the valence fluctuation one [10].

The order parameter at a volume collapse transition between two isotructural states is the trace

$$\varepsilon \equiv \mathrm{tr}\widehat{\varepsilon} = \frac{V - V_0}{V_0} \tag{1}$$

of the strain tensor $\widehat{\varepsilon}$, where V_0 is a reference volume. Our choice for V_0 as the volume at the quantum critical end point will be discussed below. The mean field theory for the KVC transition [4, 5] starts from the Gibbs free energy

$$G(p,T) = F_{\mathrm{K}}(\varepsilon, T) + pV_0\varepsilon + \frac{1}{2}BV_0\varepsilon^2 \tag{2}$$

where B is the bare (high temperature) bulk modulus that describes the elastic properties in the absence of the Kondo effect at the volume V_0. In a cubic system $B = \frac{1}{3}\left(c_{11}^0 + 2c_{12}^0\right)$ with bare elastic constants c_{11}^0 and c_{12}^0, p is the pressure, and $F_{\mathrm{K}}(\varepsilon, T)$ the Kondo contribution to the free energy. For $T \ll T_K$, $F_{\mathrm{K}}(T, V) \simeq -V_0\left(T_K + a\frac{T^2}{T_K}\right)$ with Kondo temperature $T_K \simeq De^{-1/J_K}$ (D is of order the bandwidth of the conduction electrons) and a of order unity. Due to the exponential variation of T_K with J_K, moderate variations of the Kondo coupling J_K with volume cause a strong volume dependence of the Kondo temperature. This, in turn, yields a non-linear equation of state $p(V) = -\left.\frac{\partial F}{\partial V}\right|_T = -\frac{1}{V_0}\left.\frac{\partial F}{\partial \varepsilon}\right|_T$. It is easy to verify that with appropriate values of B, even a linear volume dependence of J_K yields $p-V$ isotherms similar to those of the van der Waals theory of the liquid-gas transition [4, 5], with a first order transition where a discontinuous volume change occurs. For sufficiently large B, the line of first order transitions is terminated at a lower critical end point. For $T \gg T_K$, F_{K} is dominated by a saturating spin entropy, resulting in a termination of the line of first order transitions at a high T critical end point [16].

In order to go beyond mean field theory and to analyze the quantum critical fluctuations of the KVC transition, we consider $\varepsilon(\mathbf{x},\tau)$ as a space and time dependent fluctuating strain with a field theory governed by the action

$$S[\varepsilon] = S_{\mathrm{fl}}[\varepsilon] + \int d^dx \int_0^\beta d\tau \left(\Phi\left(\varepsilon(\mathbf{x},\tau)\right) + p\varepsilon(\mathbf{x},\tau)\right). \tag{3}$$

Here, $S_{\mathrm{fl}}[\varepsilon]$ describes strain fluctuations that are nonlocal in time and space while the static potential $\Phi(\varepsilon)$ includes the nonlinear effects of the theory. The external pressure p occurs in the last term such that the Gibbs free energy follows as $G(p) = -T\log\int d\varepsilon \exp(-S)$. We first derive Eq. 3 from a microscopic model. Then we discuss the physical consequences that follow from the analysis of $S[\varepsilon]$.

To describe the Kondo lattice physics of the system, we start from the infinite U Anderson lattice model

$$H = H_0 + \sum_{i\sigma}\left(\epsilon_f^0 f_{i\sigma}^\dagger f_{i\sigma} + t\left(f_{i\sigma}^\dagger c_{i\sigma} + h.c.\right)\right) \tag{4}$$

where $H_0 = \sum_{\mathbf{k}\sigma}\epsilon_{\mathbf{k}}c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}$ is the Hamiltonian of the conduction electrons, ϵ_f^0 the bare f electron energy, and t the hybridization. The model describes strongly correlated electrons because of the infinite Coulomb repulsion of the f electrons, leading to $n_{fi} = \sum_{\sigma=1}^N f_{i\sigma}^\dagger f_{i\sigma} \leq 1$ (N is the degeneracy of the f electrons).

In a situation where the value of the hybridization depends sensitively on the volume of the system, i.e. on the local strain ε_i, we replace $H \rightarrow H + H_{\mathrm{c}}$ with

$$H_{\mathrm{c}} = \gamma t\sum_{i\sigma}\varepsilon_i\left(f_{i\sigma}^\dagger c_{i\sigma} + h.c.\right) + \frac{B}{2}\frac{V_0}{N_0}\sum_i\varepsilon_i^2 \tag{5}$$

where γ is the coefficient of the assumed linear volume dependence of the hybridization. B is, as in Eq. 2, the bare bulk modulus and N_0 the number of unit cells in the system. In Eq. 5 we assumed that ε only couples to the hybridization. Additional couplings to the conduction band and f level energies also occur, but will not qualitatively change the conclusions of our paper. They will be ignored in what follows.

In order to obtain a quantitative insight into the low temperature behavior of the Kondo lattice, we use a slave boson mean field approach [17] to enforce the constraint $n_{fi} \leq 1$. The main results of this paper do not depend on the details of this method, though. The result of the slave boson mean field theory is the free energy $\Phi(\varepsilon)$ per volume V_0 as a function of strain. Within mean field theory $\Phi(\varepsilon) = F_K/V_0 + \frac{1}{2}B\varepsilon^2$ of Eq. 2 and results for the volume collapse transition are in full agreement with Refs. 4 and 5.

In Fig. 2 we show the results for the pressure-strain dependence of the Gibbs free energy $G(\varepsilon) = \Phi(\varepsilon) + p\varepsilon$ for different values of the bare bulk modulus as obtained from the slave boson mean field calculation. Close to the transition and at low T the potential has the form

$$\Phi(\varepsilon) = \Phi_0 - p^*\varepsilon + \frac{b}{2}\varepsilon^2 - \frac{v}{3}\varepsilon^3 + \frac{u}{4}\varepsilon^4 \tag{6}$$

Here, Φ_0 is the ε independent part of $\Phi(\varepsilon)$ and $p^*(T=0)$ the pressure at the critical point. The coefficients p^*, b, v and u can be obtained from the slave boson theory by differentiating the free energy with respect to the strain.

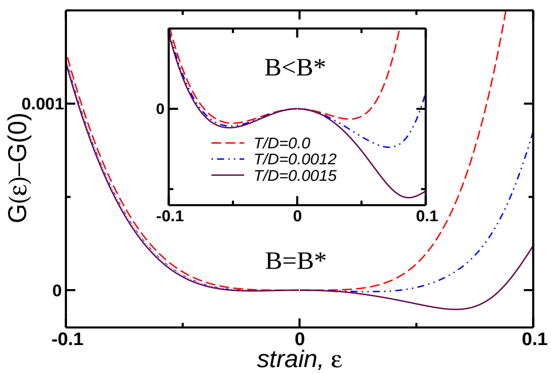

FIG. 2: Slave boson mean field results for the strain dependence of the Gibbs free energy. A double minima indicates the presence of a first order transition. For $B = B^*$ and $T = 0$, the double minima collapse to a single one, indicating the presence of a quantum critical end point. For $B < B^*$ (inset), the transition is always first order.

They are temperature dependent due to the temperature dependence of the spin entropy, and thus at low temperatures are functions of $\frac{T^2}{T_0}$, where T_0 is of order the Kondo temperature. Note that b also has a term determined by the bare bulk modulus B (Eq. 2). The lower end point of the KVC transition is located at $T = 0$, if $\frac{\partial p}{\partial \varepsilon} = \frac{\partial^2 p}{\partial \varepsilon^2} = 0$. This is achieved by varying B to the value B^* and the pressure to p^*. In order to have this transition take place at $\varepsilon = 0$, we choose the so far arbitrary reference volume V_0 such that $\Phi(\varepsilon)$ has no contribution of order ε^3 at $T = 0$. This implies that $v = \varkappa T^2/T_0$ with $\varkappa > 0$ and that p^* now depends on B.

The dynamic and nonlocal part S_{fl} of the action can also be derived within the slave boson approach. Integrating out the fermionic degrees of freedom,

$$S_{\text{fl}} = \frac{1}{2}\int_q (\Pi(q) - \Pi(0)) |\varepsilon(q)|^2 \tag{7}$$

where $\int_q \dots = T\sum_n \int \frac{d^d\mathbf{q}}{(2\pi)^d} \dots$ with $q = (\mathbf{q},\omega_n)$ and $\Pi(q) = -N\gamma^2 t^2 \int_{q'} \left(G^{cc}_{q'} G^{ff}_{q'+q} + G^{cf}_{q'} G^{cf}_{q'+q}\right)$. The polarization bubble $\Pi(\mathbf{q},\omega)$ determines the dynamics of the strain field and is determined by the single particle propagators of the fermions within the slave boson calculation, i.e. $G^{cc}_{\mathbf{q}}(\tau) = -\left\langle T_\tau c_{\mathbf{q}}(\tau) c^\dagger_{\mathbf{q}}(0)\right\rangle$, etc. The evaluation of this expression for small $\mathbf{q}$ and ω (but with $v_F|\mathbf{q}| \gg \omega$) yields[18]

$$S_{\text{fl}} = \frac{1}{2}\int_q \left(\Gamma\frac{|\omega_n|}{v_F|\mathbf{q}|} + \left(\frac{\alpha\mathbf{q}}{2k_F}\right)^2\right)|\varepsilon(q)|^2 \tag{8}$$

As long as the system is in a heavy fermi liquid regime, the generic ω and $\mathbf{q}$-dependence of S_{fl} in Eq. 8 is independent of the details of the slave boson approach. The latter does however allow one to determine the prefactors Γ and α in terms of microscopic quantities[17, 18]. The model, Eqs. 3 and 8, is essentially the same as the one used by Millis *et al.* [8] in the context of metamagnetic quantum criticality in metals and numerous analogies exist.

From the effective action, Eqs. 3, 6 and 8, we obtain the equation of state including fluctuation corrections and determine the location of the volume collapse transition. It follows that

$$p = p^* - \left(b + u\left\langle\varepsilon^2\right\rangle\right)\varepsilon + v\varepsilon^2 - u\varepsilon^3 \tag{9}$$

with $\left\langle\varepsilon^2\right\rangle_{B=B^*} = \int_q \left(\frac{\Gamma|\omega_n|}{v_F|\mathbf{q}|} + \left(\frac{\alpha\mathbf{q}}{2k_F}\right)^2\right)^{-1}$. There are two distinct sources of temperature variation in Eq. 9. First, due to the temperature dependence of the mean field entropy, it holds for $T \ll T_0$: $p^*(T) = p^*_0 + \zeta'\frac{T^2}{T_0}$, $b(T) = b_0 - \zeta\frac{T^2}{T_0}$, etc., where ζ, ζ' are positive constants. Second, the order parameter fluctuations are temperature dependent: $\left\langle\varepsilon^2\right\rangle_T = \left\langle\varepsilon^2\right\rangle_{T=0} + \tilde{\zeta}T^{\frac{d+1}{3}}$ with $\tilde{\zeta} \simeq \frac{12.15\Gamma^{1/3}}{\alpha^{8/3}(v_F k_F)^{1/3}} > 0$ for $d = 3$. For $d < 5$, the latter is the dominant effect (fluctuation corrections due to the cubic term $\propto v$ are subleading).

We first ignore the T dependence of $\left\langle\varepsilon^2\right\rangle$, formally corresponding to $d > 5$, and analyze the mean field $p - T$ phase diagram. The critical end point is located at $T = 0$ if $p = p^*_0$ and $B - B^* \equiv b_0 + u\left\langle\varepsilon^2\right\rangle_{T=0} = 0$. Close to this transition at $T = 0$, $\varepsilon(B = B^*, p) \propto (p^*_0 - p)^{1/3}$ and $\varepsilon(B, p = p^*_0) \propto (B^* - B)^{1/2}$. At finite T we obtain a first order transition if $B < B^* + \zeta\frac{T^2}{T_0}$. For $B > B^* + \zeta\frac{T^2}{T_0}$, no transition takes place. The zero temperature transition is first order for $B < B^*$, second order for $B = B^*$, and absent for $B > B^*$. For the following set of parameters: $t = 0.5$eV, $D = 1$eV, $\varepsilon^0_f = -2.34$eV, (yielding $T_K \simeq 0.012D$ and $n_f = 0.87$), $B^* = 254$kbar, $p^*_0 = -4.7$kbar and $\gamma = 2.14$, the corresponding $p - T$ curves are shown in the inset of Fig. 1. The value for γ is chosen to yield results that quantitatively reproduce the mean field theory of Ref.[4].

The phase diagram changes qualitatively if we include the temperature dependence of the critical fluctuations of the order parameter $\left\langle\varepsilon^2\right\rangle_T$, which is dominant at low temperatures for $d < 5$. Besides entering with a different power than the mean field terms, the key new aspect of this fluctuation effect is that it leads to an increase, as opposed to a decrease, of the $b(T) + u\left\langle\varepsilon^2\right\rangle$ term in Eq. 9 as T increases. While the mean field entropy softens the bulk modulus, critical fluctuations harden it. Thus, if the critical point is located at $T = 0$, increasing temperature will suppress the transition rather than making it go first order. This effect is demonstrated in Fig. 1, where we show the fluctuation corrected transition lines for different bulk moduli. The competition between the fluctuation term (which dominates at the lowest temperatures)

and the mean field terms (which dominate at higher temperature) leads to the development of a gap in the first order line at a $B > 0.9683B^*$. With increasing B, the first order line below this gap eventually collapses to a quantum critical point at $B = B^*$, and then disappears for larger B. Thus, the critical end point becomes isolated in the $p-T$ phase plane. For the parameters we used, the gap in the first order transition $\simeq 0.002D \simeq 20$K should be observable.

Next, we use the equation of state Eq. 9 close to the quantum critical end point to determine the pressure and temperature dependence of ε, the compressibility κ and the thermal expansion β. The analysis of Eq. 9 yields

$$\begin{aligned} \varepsilon &= \frac{\Delta V}{V} \propto T^{\phi},\ \kappa = -\frac{1}{V}\frac{\partial V}{\partial p} \propto T^{-\gamma} \\ \beta_T &= \frac{1}{V}\frac{\partial V}{\partial T} \propto T^{-\theta} \end{aligned} \tag{10}$$

where $\theta = 1-\phi$. We obtain the exponents $\phi = \frac{2}{3}$, $\gamma = \frac{4}{3}$ and $\theta = \frac{1}{3}$ for $d \geq 3$ and $\phi = \frac{5-d}{3}$, $\gamma = \frac{d+1}{3}$ and $\theta = \frac{d-2}{3}$ for $d < 3$. For $d < 3$ the T-dependence of the strain is governed by the fluctuation corrections in the equation of state, while for $d > 3$, the mean field T dependence $\frac{T^2}{T_0}$ in $\Phi(\varepsilon)$ of Eq. 6 dominates. For $d = 3$ both terms yield exactly the same T dependence. The strain fluctuations also give rise to a singular heat capacity $\frac{C_V}{T} \propto -\log T$ for $d = 3$ and $\frac{C_V}{T} \propto T^{\frac{d-3}{3}}$ for $d < 3$. For the physically relevant heat capacity at constant pressure $C_p = C_V + V\kappa T\left(\partial p/\partial T\right)_V^2$ we find $C_p - C_V \propto T^{3-\gamma}$, i.e. the dominant contribution to C_p comes from C_V. Pressure tuning at $T = 0$ yields a diverging compressibility: $\kappa \propto |p - p_0^*|^{-2/3}$. Critical fluctuations in the charge sector furthermore yield non-Fermi liquid behavior of the single particle self energy: $\Sigma_{k_F}(\omega) \propto \omega\,|\omega|^{-\frac{3-d}{3}}$ for $d < 3$ and $\Sigma_{k_F}(\omega) \propto \omega \log|\omega|$ for $d = 3$.

Finally we comment on the possibility of superconductivity caused by the interaction of electrons with these critical fluctuations. Strain fluctuations couple to electrons just like phonons or other bosonic charge excitations, leading to an attractive interaction in the s-wave pairing channel. Superconductivity as caused by valence fluctuations was discussed in Refs. 9 and 10. In those treatments, retardation effects of the pairing interaction enter the theory solely via the upper cut off, ω_0, of the theory. In the weak coupling limit this leads to the well known BCS-formula for the transition temperature $T_c^{BCS} \simeq \omega_0 e^{-\frac{1}{\lambda_p}}$ where $\lambda_p \propto \frac{\gamma^2 t^2}{D^2}$ is the dimensional coupling constant of the pairing interaction. However, in the vicinity of the critical end point, the strain fluctuations serve as pairing boson which becomes massless. As shown in Ref. 19, 20 retardation effects are more subtle in the case of pairing due to a massless boson governed by Eq. 8. For a given value of λ_p, the transition temperature is enhanced compared to the BCS result and it follows that

$$T_c \simeq \omega_0 e^{-\frac{\pi}{2\sqrt{\lambda_p}}}. \tag{11}$$

Thus, the critical fluctuations discussed in this paper are good candidates for bosons that cause s-wave superconductivity.

In summary, we have analyzed the critical behavior in the vicinity of a $T = 0$ end point for the Kondo volume collapse transition. We find diverging specific heat and thermal expansion coefficients, and a diverging compressibility. We also find that critical fluctuations break apart the line of first order transitions, leading to a novel "isolation" of the critical end point in the pressure-temperature phase plane. Finally, we discussed the implications of our results for the existence of superconductivity near a KVC quantum critical end point.

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is the density of states at the Fermi level, m^* and $(k_F/k_{0F})^2 = 1 + (1 - n_f)\, t^2 / \left(\epsilon_f^0 D\right)$ are the renormalized mass and Fermi momentum of the heavy quasiparticles below T_K.

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